Prof. Peckham, of Ann Arbor, read a paper on "The Nature and Origin of Petroleum."

A communication from Mr. David T. Day was read, entitled "A Suggestion as to the Origin of Pennsylvania Petroleum."

The Secretary read by title two papers by Prof. Phillips on "The Genesis of Natural Gas and Petroleum," and on "The Occurrence of Petroleum in the Cavities of Fossils."

Prof. Mabery then presented his views on the composition of Petroleum.

Remarks in discussion were then made by Dr. Sadtler, Mr. Wharton, Prof. Mabery and Prof. Peckham, and Prof. Mabery closed the discussion with a warm recognition of Dr. Sadtler's and Prof. Peckham's work.

THE GENESIS AND CHEMICAL RELATIONS OF PETROLEUM AND NATURAL GAS.

BY SAMUEL P. SADTLER, PH.D.

(*Read February 5, 1897.*)

Of natural products in the mineral kingdom, few have excited the interest of geologists and chemists in the same degree as what in the broad sense we call bitumen. Occurring as it does in solid, liquid and gaseous condition in almost all parts of the world, and in amount varying from the slight bituminous impregnation of shales, limestones, sandstones, and other rocks to the great petroleum deposits which are now worked in this country and Russia, it has furnished ever-new and interesting material for scientific study and discussion.

This widespread occurrence and the varied forms under which it is brought to our attention would be quite sufficient to explain its interest from a geological point of view, but when we add to this that in its main forms of production, petroleum and natural gas, chemists find represented those simplest forms of organic compounds, the hydrocarbons, we have an additional element of interest.

Under these circumstances, it would be hard for the scientific student to refrain from theorizing as to the origin and conditions of formation and storage in nature of this great class of products. And if these theories already possessed interest in the earlier half of this century, might we not suppose that the great economic value which petroleum and natural gas have attained in the last few decades would add greatly to this? The question has indeed become a very large one, and the mass of literature pertaining thereto has already become so great that it would be impossible in the brief limit of time assigned me to cover it even in outline. Leaving therefore the broad subject of natural bitumens, it has been thought well to take for such discussion, as time allows, the narrower question of "the origin and chemical character of petroleum." And as the Society is honored this evening by the presence of several gentlemen who are known by contributions already made to this question, and have consented to favor us with papers specially prepared for this occasion, I shall merely state in brief outline the several well-known theories that have been advanced from time to time, and add an account of some experimental results that I have myself obtained which I think will have a bearing upon some of the views now held.

The theories as to the origin of petroleum may be divided broadly into those which attribute it to Inorganic Sources and those which consider it to be derived from Organic Sources. Under the first of these heads, we may again distinguish between the theories which consider it merely as a natural emanation and those which attribute it to the result of definite chemical reactions.

The first suggestion of the emanation theory for the origin of petroleum seems to have come from Alexander von Humboldt, who in 1804, in describing the petroleum springs in the Bay of Cumaux on the Venezuelan coast, throws out the suggestion that "the petroleum is the product of a distillation from great depths and issues from the primitive rocks, beneath which the forces of all volcanic action lie." Rozet (1835), Prott (1846), Parran (1854), and Thoré (1872), in writing upon the asphalt and petroleum occurrences in France, all seemed inclined to connect these formations with volcanic, or at least igneous and eruptive, agencies.

Somewhat similar was the theory advanced by the French geologist Coquand, who, because of the association of mud volcanoes with the occurrence of petroleum in Sicily, the Apennines, the peninsula

of Taman and the plains of Roumania, concluded that mud volcanoes produced petroleum and other forms of bitumen by converting marsh-gas into more condensed hydrocarbons. This derivation of liquid and even solid bitumens like ozokerite from marsh-gas as an original source was also advanced as a theory by Grabowski, who has made special studies on Galician ozokerite.

The simplest of the emanation theories, however, is that of the Russian geologist Sokoloff, who believes that petroleum is a cosmic product, formed in the crust of the earth as bitumens are formed in meteorites and comets by direct union of the elements hydrogen and carbon. According to this theory, the liquid and solid bitumens represent successive stages in the condensation and oxidation of simpler gaseous hydrocarbons.

These emanation hypotheses do not find much acceptance at present. The connection between the petroleum occurrence and volcanic activity or hot springs seems to be far from general, and may indeed be classed as local and fortuitous; the oil does not issue from the earth at any higher temperature than that of the surface, as it might be expected to if connected with deep-seated volcanic or cosmic activity; and lastly, the most abundant oil deposits are not located in the regions where upheaval and fracture of the earth's crust show most strongly.

More interest perhaps has been awakened by the theories of inorganic origin which involve definite chemical reactions. Foremost among these was that of Berthelot, who, in 1866, advanced the theory that the interior of the earth contained free alkali metals, and that these, when acted upon by carbonic acid or an earthy carbonate at high temperatures, would form acetylides or carbides of the alkali metals which decompose with water to form hydrocarbons analogous to those found in petroleum. If, then, water containing carbonic acid gas were to reach these metallic masses by infiltration and act upon them at high heat and under pressure, both liquid and gaseous hydrocarbons would result. The production of metallic carbides as a product of the electric furnace, and their ready decomposition for the production of acetylene gas, now carried out on a commercial scale, has added new interest to this theory of Berthelot's.

This line of hypothesis was farther developed by Byasson in 1871, who obtained petroleum-like products by the action of steam and carbonic acid gas upon iron and its sulphide at a high tempera-

ture. Cloez, in 1877, also obtained petroleum-like hydrocarbons by the action of dilute acids, and even of boiling water, upon the carbides of iron such as exist in spiegeleisen. In the paper of the Russian chemist Mendelejeff, however, published also in 1877, this theory is most fully elaborated. The existence of metallic carbides in the depths of the earth he considers likely from the fact that similar carbides are found in meteorites, and that metallic iron may occur in large deposits in the interior of the earth he considers possible, because the mean specific gravity of the earth, 5.5, is notably higher than that of ordinary rock material. If, then, water be supposed to have infiltrated through fissures in the earth's crust, we have the conditions shown by experiment as capable of yielding petroleum-like hydrocarbons. The same steam which, acting upon the metal or metallic carbide, was capable of forming the petroleum, could also force its vapors when formed through the fissures until on cooling they condensed and were absorbed in strata capable of holding them in liquid form. The eminent geologist Abich, who had made a study of the Caucasian oil field, also joined in the acceptance of this theory of Mendelejeff, and it may be said to be the one of the inorganic theories that has found the most general indorsement.

The great preponderance of belief is, however, at the present time against this or any other theory based upon purely inorganic materials or reactions. The entire absence of petroleum from the archaic formations, from which traces of fossil life are also absent, and the occurrence of the petroleum in sedimentary formations which have been free from any volcanic or metamorphic disturbance, go to render these emanation theories improbable. The fact, moreover, that while the hydrocarbons of petroleum show a range of temperature of condensation from 0° to 300°, which would necessarily distribute them in different strata if they rose from the interior in vapor form, we find them all, from the highest to the lowest, admixed in one and the same oil-bearing formation, also speaks against the probability of the theories stated above.

Turning now to the theories of the organic origin of petroleum, we note first the belief that it comes essentially from vegetable sources. Thus Prof. Lesquereux considered that the Pennsylvania oil was formed from the remains of marine algæ, because the Devonian shales which accompany the oil formation contain an abundance of fossil fucoids. It is pointed out, however, by Höfer and

other critics of this theory that in many localities fucoid remains are abundant without a trace of bituminous products accompanying them.

E. W. Binney having observed petroleum oozing from a decomposing bed of peat in England, which had been covered in with sand, considered that it came from a decomposition of the peat out of access of air. However, it has been pointed out that this was an isolated observation, and that in many other peat bogs similarly covered no evidence of petroleum has been found.

Wall and Kruger, after studying the asphalt occurrence in the island of Trinidad, proposed the theory that asphalt and petroleum were formed by the decomposition of woody fibre, of which they found abundant traces in the asphalt deposits. A later observer, Rupert Jones, however, on extracting Trinidad asphalt with hot turpentine found animal remains so clearly that a derivation from these is at least as probable.

We may mention also the earlier views of Reichenbach, who viewed petroleum as formed by a destructive distillation of vegetable remains simultaneously with the formation of the coal deposits, but in answer to this it is only necessary to note that the petroleum and the coal do not occur together in the majority of instances and that petroleum differs essentially in chemical composition from either wood-tar or coal-tar as ordinarily obtained.

The eminent French geologist, Daubrée, also found a vegetable origin for petroleum. He says that "it appears not to be a simple product of dry distillation, but to have been formed with the concurrent action of water and perhaps under pressure." He adduces in support of his view the fact that by the action of superheated steam upon wood he had obtained both liquid and gaseous products analogous to petroleum.

The belief in the animal origin of petroleum has had advocates equally as positive and persistent. In this country, J. D. Whitney, the former State Geologist of California, and T. Sterry Hunt, who was well acquainted with both the Canadian and Pennsylvania oil fields, were its chief advocates. The latter has produced many strong illustrations in his study of Canadian formations of his view that fossiliferous limestones, the remains in which are mainly if not exclusively of animal origin, were the original beds in which the petroleum was formed.

In Europe, the most prominent advocates of the animal origin of

petroleum have been Höfer and Engler. The former of these writers in his work, *Das Erdoel und seine Verwandten,* published in 1888, summarizes the arguments for believing petroleum to be of animal origin as follows:

1. We find petroleum in original deposits with animal remains, but not or with only the smallest traces of vegetable remains, as for example in the fish shales of Carpathia and the limestones of Canada studied by T. Sterry Hunt.

2. Shales which, on account of their high per cent. of bitumen, are adapted for the production of oil or paraffine, are also rich in animal and poor or entirely void of vegetable remains, as for example the bituminous shales of the Lias formation in Swabia and Steierdorf (Banat). The copper-bearing shales of Mansfield, which contain as high as twenty-two per cent. of bituminous matter, also carry an abundance of animal remains, but only very rarely any vegetable remains.

3. Rocks which are rich in vegetable remains as a rule are not bituminous, but they become so if animal remains accompany the other.

4. By the decomposition of animal remains it is possible to form hydrocarbons analogous to those of petroleum oils.

5. O. Fraas observed petroleum oozing from a coral bank on the borders of the Red Sea, where it could only have had an animal origin.

The fact that origin from animal remains makes it necessary to account for the nitrogen, is met by the fact that most asphalts and bitumens, including petroleum, do contain nitrogen. That they do not contain more is explained, according to Höfer, by the circumstance that the nitrogen is lost in volatile compounds like ammonia. Of course animal remains are found in many formations that do not contain bitumen or petroleum, but the conditions may have been unfavorable for its accumulation and retention in these cases. The actual formation of petroleum-like compounds from animal products had been carried out experimentally some years before Höfer's publication, by our countrymen, Warren and Storer, who distilled the lime soap of menhaden (fish) oil, and obtained members of the methane, ethylene and benzene series of hydrocarbons, such as are found in petroleum.

However, Höfer's theory was taken up as the suggestion for experimental study by Engler, of Carlsruhe, and at his hands it

has received a more definite statement. Engler distilled 490 kilos. of menhaden oil at a temperature beginning at 320° C. under a pressure of ten atmospheres, and increasing to 400° under a pressure of four atmospheres. He obtained about sixty per cent. of an oil distillate of 0.815 specific gravity. Thirty-seven per cent. of the distillate was taken out by shaking with sulphuric acid, indicating unsaturated hydrocarbons, while the remainder yielded, on fractional distillation, pentane, hexane, normal and secondary hexane, normal octane and nonane. A burning oil fraction was separated, and in his latest experiments solid paraffine was also obtained from the heavier portions. Prof. Engler gave a *resumé* of his experimental results at the World's Fair Congress of Chemists, in Chicago, in August, 1893, and I had the pleasure of hearing it and examining his specimens at that time. In consequence of this work of Engler, which he extended later to lard oil as well as to menhaden oil, and to artificial tri-oleines as well, the belief in the animal origin of petroleum has become quite the prevalent one.

Let us, however, take up for a moment the idea of the joint animal and vegetable source. This joint origin was advocated first of all by Prof. J. P. Lesley, the Director of the Second Geological Survey of Pennsylvania, and an honored Vice-President of this Society. He believes that "it is in some way connected with the vastly abundant accumulations of Paleozoic sea weeds, the marks of which are so infinitely numerous in the rocks, and with the infinitude of coralloid sea animals, the skeletons of which make up a large part of the limestone formations which lie several thousand feet beneath the Venango oil-sand group." The same view was held by the late C. A. Ashburner, of the Pennsylvania Geological Survey.

Prof. Edward Orton, of the Ohio Survey, summarizes his views in the following postulates: (1) Petroleum is derived from organic matter; (2) Petroleum of the Pennsylvania type is derived from the organic matter of the bituminous shales and is probably of vegetable origin; (3) Petroleum of the Canada type is derived from limestones and is probably of animal origin.

Prof. Peckham, in his report on Petroleum for the Census of 1880, also makes a distinction in the origin of different classes of petroleums. He divides all bitumens into four classes:

1. Those bitumens that form asphaltum and do not contain paraffine.

2. Those bitumens that do not form asphaltum and contain paraffine.

3. Those bitumens that form asphaltum and contain paraffine.

4. Solid bitumens that were originally solid when cold or at ordinary temperatures.

"The first class includes the bitumens of California and Texas, doubtless indigenous in the shales from which they issue. The exceedingly unstable character of these petroleums, considered in connection with the amount of nitrogen that they contain and the vast accumulation of animal remains in the strata from which they issue, together with the fact that the fresh oil soon becomes filled with the larvæ of insects to such an extent that pools of petroleum become pools of maggots, all lend support to the theory that the oils are of animal origin.

"The second class of petroleums include those of New York, Pennsylvania, Ohio and West Virginia. These oils are undoubtedly distillates and of vegetable origin. The proof of the statement seems overwhelming."

Leaving the question of origin for the present with this rapid survey of the views of the more prominent writers on the subject, and reserving for the end of this paper the mention of some few experimental results of my own which bear on it, I will briefly allude to the other question of the conditions of formation of the bitumen or petroleum. Here of course we practically leave the theories of inorganic origin to one side and assume that its source is organic. Was it formed where it is now found *in situ* or is it a distillate from lower-lying formations?

As already stated, Sterry Hunt believed that the fossiliferous limestones were the source of the Canadian oil, and he also strenuously insisted that they were formed in this same formation and did not come into it from an outside source. This view of the production of the petroleum *in situ* is also in the main supported by Profs. Lesley and Orton, although both seem to admit that under some circumstances a modified distillation takes place. The latter says: "Different fields have different sources. We can accept without inconsistency the adventitious origin of the oil in Pennsylvania sandstones and its indigenous origin in the shales of California or in the limestones of Canada, Kentucky or Ohio." On the other hand, Profs. Newberry and Peckham have advocated the theory that the oils of New York, Pennsylvania, West Virginia and Ohio at least

were products of a slow fractional distillation. Prof. Newberry speaks of black Devonian shales as the source of supply in this process, while Prof. Peckham takes in both beds of shale and limestone containing fucoids and animal remains as subjected to the distillation process.

In concluding, I have a small contribution to offer to the experimental data which bear upon the question of possible origin, and upon which we can theorize as to conditions of formation.

Engler, as already mentioned, distilled menhaden oil under pressure, and afterwards extended his experiments to lard oil and artificial oleins. From his results he is led to believe in the exclusively animal origin of petroleum. I have found that linseed oil, and presumably the other vegetable seed oils, may be made to yield similar products, and have even obtained solid paraffine from this source. While it has long been known that inflammable vapors are given off when linseed oil is boiled for varnish making and similar purposes, very little attempt has been made to collect and study the composition of these vapors. Schædler, in his exhaustive work on the vegetable and animal oils, simply makes the statement that small quantities of hydrocarbons are present in the vapors resulting from this destructive distillation.

Finding that in one case that came under my attention linseed oil was being boiled for varnish making under pressure, and that considerable quantities of a liquid distillate were being condensed in the dome of the large still and returned to the body of the oil, I arranged for the collection of these condensed vapors and collected them for examination.

At first the odor of acrolein was very pronounced and powerful, showing that the glycerine of the glycerides composing the oil was being decomposed; later the odor was more that of a cracked petroleum oil, showing that the linoleic and other acids of the oil were undergoing decomposition. The raw distillate collected after this acrolein odor had nearly disappeared, I found had a specific gravity of 0.860 and had changed so thoroughly from the original linseed oil that it showed a saponification equivalent of only 1.09, indicating that it was mainly a neutral oil and presumably made up largely of hydrocarbons. I might say here that I examined the linseed oil which was used in this test. It was a clear "old process" oil, of specific gravity 0.929, and showed a saponification equivalent of 183, which is normal for linseed oil.

The distillate above referred to was then redistilled from a small iron retort and two fractions collected, leaving a residue in the retort which had the appearance and odor of a reduced petroleum oil or residuum, such as is used in the manufacture of vaseline and similar products.

The two fractions were found to resemble what are known as paraffine oils in considerable degree, showing the characteristic fluorescence of these. They were given a partial treatment with sulphuric acid and the results are shown. From a portion of one of these fractions, on chilling in a freezing mixture, scale paraffine was also separated, of which a sample is shown. Of course the fractions must be obtained on a sufficiently large scale to admit of thorough purifying before the character of the hydrocarbons can be studied. At present they contain impurities such as aldehyde-like and possibly ketone products. They reduce ammoniacal silver solutions and indicate thus the presence of these impurities.

These results, which of course are only preliminary, are sufficient to show that we have hydrocarbon oils analogous to the natural petroleum or mineral oils formed when linseed oil is distilled under pressure. It is difficult then to see how we can avoid widening Engler's theory so as to include the vegetable seed oils as probable additional sources of petroleum. Moreover, I see no reason, if lard oil will yield the results which Engler has obtained, to doubt that vegetable oleins like olive oil and its class may also be found to be capable of the same changes.

We are thus brought from an experimental point of view to come to the acceptance of the theory of the joint animal and vegetable origin of petroleum that the majority of geologists have settled upon as according best with their study of its local occurrence.